

# Fourier Transform Spectroscopy of the Red and Orange Band Systems of Calcium Hydride

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## ABSTRACT

The spectrum of calcium hydride has been extended to include the  $\Delta v = -1$  sequence of the  $A^2\Pi - X^2\Sigma$  band and the 2-3 band of the  $B^2\Sigma - X^2\Sigma$  band system, enabling a better determination of the deperturbed vibration-rotation parameters for the  $X^2\Sigma$ ,  $A^2\Pi$ , and  $B^2\Sigma$  states. A global fit has been performed with a Hamiltonian in which the near degenerate  $B'^2\Sigma$  electronic state has been removed from the Van-Vleck summation of the  $\Lambda$ -type doubling parameters and is included directly in the Hamiltonian. A standard deviation of  $0.058\text{ cm}^{-1}$  is obtained for the nonlinear least square fit of 2129 lines.

**Keywords** CaH electronic spectrum, centrifugal distortion parameters.

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## 1. INTRODUCTION

Calcium hydride has been the subject of many spectroscopic studies due to its astrophysical interest, beginning with its identification in solar and stellar spectra. Rotational analyses of the  $A^2\Pi - X^2\Sigma$  (Red),  $B^2\Sigma - X^2\Sigma$  (Orange),  $C^2\Sigma - X^2\Sigma$ ,  $D^2\Sigma - X^2\Sigma$  (Blue-green), and  $E^2\Pi - X^2\Sigma$  (Blue) transitions have provided considerable insight into molecular structure and spectroscopy, and have been used to make CaH a hydride prototype case study (Herzberg (1950)).

Recently it has become the focus of considerable experimental and theoretical investigations owing to the recognition of significant perturbations in the electronic structure and spectrum due to the presence of a double minimum in the B-state potential energy curve (Berg and Klynning (1974, 1974a), Berg, Klynning and Martin (1976), Klynning and Martin (1981)). Multiple minima in potential energy curves can result when avoided crossings between potential curves of different electronic states occur. In this case a repulsive neutral electron configuration crosses through two different attractive ionic electronic configurations. The resulting electronic structure is a mixture of the three configurations, which bears little resemblance to the typical asymmetric harmonic oscillator potentials (Shida, Tanaka, and Ohno (1987), Chambaud and Levy (1989)).

The present work expands on the work of Martin (1984) with a simultaneous deperturbation analysis of the red and orange band systems to obtain molecular parameters for the  $X^2\Sigma$ ,  $A^2\Pi$ ,  $B^2\Sigma$ , and  $B'^2\Sigma$  electronic states. In the present work the  $\lambda$ -type doubling is included explicitly and the result is an order of magnitude improvement in the standard deviation of the global fit. Nevertheless, the fact that the standard deviation is considerably larger than the uncertainty in the measurement of the line positions indicates that some refinement of the theoretical model remains to be done.

## 2. EXPERIMENTAL

The source was a commercial King furnace operated at temperatures from 1475 to 1760 K, filled with hydrogen at a pressures from 200 to 500 torr. Special care was taken to operate the furnace within a temperature range that produced measurable absorption in both the A-X and B-X transitions without permitting saturation in any of the stronger spectral lines. The spectrometer was the McMath Fourier transform spectrometer at the National Solar Observatory, Kitt Peak, set to a resolving limit of  $0.034\text{ cm}^{-1}$ , and a

wavenumber range of 14000 to 16000  $\text{cm}^{-1}$ . The interferogram was the sum of twenty to thirty scans over a period of an hour, which produced a signal-to-noise ratio of about 200 for the strongest CaH lines.

A line list was generated from the transformed interferogram using the interactive data-processing code DECOMP written by Brault, and adapted for use with IBM PC-compatible computers (Brault and Abrams (1988)). Each identifiable CaH line, when absorption was changed to absorbance, was fitted with a Voigt function to obtain accurate estimates of the wavenumber, intensity, width, damping parameter and equivalent width. The doublet splitting was observable, although many of the lines were blended.

For the 2129 lines identified and fitted the mean error in line position when fitting branches was 20 mK which is somewhat large for line widths of 100 mK and signal to noise ratios of 2 to 200. Absolute wavenumber calibration was made from the stabilized laser interferometer control, without comparison to internal standards. The wavenumbers and J-value assignments for the newly observed lines of the A-X (Red) system are given in Table 1, and for the lines of B-X (Orange) system in Table 2. The identification of all other transitions is consistent with the works of Martin (1984) and Klynning and Martin (1979).

### 3. THEORY

Effective Hamiltonians for the interpretation of the spectra of diatomic molecules begin with approximating the exact Hamiltonian by

$$H = H_0 + H_{ROT} + H_{FS} + H_{LD} + H_{CDLD} \quad (1)$$

where  $H_0$  includes all the rotation independent terms of the Born- Oppenheimer approximation and involves only electronic and vibrational quantum numbers. The hyperfine splitting is unresolved in the infrared and consequently the hyperfine interaction terms have been omitted.  $H_{ROT}$  is the rotational energy and  $H_{CD}$  includes the centrifugal distortions of the rotational energy. The term  $H_{FS}$  describes the fine structure interactions and  $H_{LD}$  and  $H_{CDLD}$  describe the lambda doubling interaction and its centrifugal distortion respectively. The rotational Hamiltonian  $H_{ROT}$  is

$$H_{ROT} = B(r)\mathbf{R}^2 - D(r)\mathbf{R}^4 + H(r)\mathbf{R}^6 \quad (2)$$

where

$$B(r) = \frac{\hbar^2}{2\mu r^2} \quad (3)$$

is the radial part of the rotational energy operator  $H_{ROT}$ ,  $\mu$  is the reduced mass and  $r$  is the internuclear distance.  $D(r)$  and  $H(r)$  are the quartic and sextic corrections to  $B(r)$ . The first-order rotational energy operator  $B(r)\mathbf{R}^2$  can be evaluated using Hund's coupling case (a), where the operator  $\mathbf{R}$  represents the angular momentum of the rigid nuclear framework, yielding

$$\begin{aligned} B(r)\mathbf{R}^2 &= B(r)[(\mathbf{J} - \mathbf{L}) - \mathbf{S}]^2 \\ &= B(r)[(\mathbf{J}^2 - J_Z^2) + (\mathbf{L}^2 - L_Z^2) + (\mathbf{S}^2 - S_Z^2) \\ &\quad - (J_+L_- + J_-L_+) - (J_+S_- + J_-S_+) + (L_+S_- + L_-S_+)] \end{aligned} \quad (4)$$

where the  $\pm$  subscripts indicate angular momentum raising and lowering operators. The fine structure Hamiltonian has three phenomenological components

$$H_{FS} = H_{SS} + H_{SO} + H_{SR} \quad (5)$$

where the spin-spin interaction energy is rigorously zero for doublet states, the spin-orbit interaction is

$$H_{SO} = A(r)\mathbf{L} \cdot \mathbf{S} + \frac{1}{2}A(r)(L_+S_- + L_-S_+) \quad (6)$$

and

$$H_{SR} = q(r)(\mathbf{J} - \mathbf{L} - \mathbf{S}) \cdot \mathbf{S} \quad (7)$$

is the spin-rotation interaction energy operator. For off-diagonal matrix elements the terms involving raising and lowering operators include perturbations that are included at higher order in the microscopic Hamiltonian. In the preceding discussion interactions that couple different electronic states were neglected. However, interactions between  $\Sigma$  and  $\Pi$  states of the same multiplicity produce the lambda doubling splitting which remove the degeneracies of the  $\Lambda$  components of the  $^2\Pi$  state. We use three lambda-doubling parameters, following Mulliken and Christy (1931),  $o_V$ ,  $p_V$ , and  $q_V$  (defined in Table 3) and focus on terms of the rotational and fine structure Hamiltonians  $H_{ROT}$  and  $H_{FS}$  that contribute to interactions between the  $^2\Sigma$  and  $^2\Pi$  states.

The lambda-doubling Hamiltonian has the form

$$H_{LD} = -B(r)(J_+L_- + J_-L_+) + [B(r) + \frac{1}{2}A(r)](L_+S_- + L_-S_+). \quad (8)$$

A Van Vleck transformation may be used to "fold in" the combined effects of the perturbing states as a correction to the matrix elements of the Born-Oppenheimer states we can replace equation (8) with an effective lambda-doubling Hamiltonian

$$H_{LD}^{(v)} = \frac{1}{2}q_V(J_+ + J_-)^2 - (\frac{1}{2}q_V + \frac{1}{4}p_V)[(J_+ + J_-)(S_+ + S_-) + (S_+ + S_-)(J_+ + J_-)] + (\frac{1}{2}q_V + \frac{1}{2}p_V + o_V)(S_+ + S_-). \quad (9)$$

The Van Vleck transformation can be used to generate higher-order corrections to account for the centrifugal distortion of the molecule as it rotates. Definitions of the effective higher order parameters are given in Table 3. The sextic centrifugal distortion  $H$  results from a third-order Van Vleck correction to the rotational energy; as does the centrifugal correction to the lambda-doubling parameters generates  $p_D$  and  $q_D$ . In fourth-order the significance of many terms becomes poorly determined and only  $q_H$  is included in our analysis. At this level the physical significance of the terms is obscure at best and in practice the parameters are retained simply to introduce a particular  $J$ -dependence in the Hamiltonian as suggested in equation (2).

The matrix elements of the unique perturber approximation Hamiltonian are evaluated using a basis set of Hund's case (a) wavefunctions that are simultaneous eigenfunctions of  $J^2$ ,  $S^2$ ,  $J_z$ ,  $S_z$  and  $L_z$  with corresponding eigenvalues  $J(J+1)$ ,  $S(S+1)$ ,  $\Omega$ ,  $\Sigma$ , and  $\Lambda$ . The complete wavefunction is a product of an electronic-vibrational wavefunction  $|n, v\rangle$  and the case (a) wavefunction  $|\Lambda\Sigma S\Omega J\rangle$  symmetrized with respect to reflection in the plane containing the internuclear axis. In the analysis of CaH three symmetrized wavefunctions are necessary

$$|^2\Sigma_{1/2e/f}\rangle = \frac{1}{\sqrt{2}}(|^2\Sigma_{1/2}\rangle \pm |^2\Sigma_{-1/2}\rangle) \quad (10a)$$

$$|^2\Pi_{1/2e/f}\rangle = \frac{1}{\sqrt{2}}(|^2\Pi_{1/2}\rangle \pm |^2\Pi_{-1/2}\rangle) \quad (10b)$$

$$|^2\Pi_{3/2e/f}\rangle = \frac{1}{\sqrt{2}}(|^2\Pi_{3/2}\rangle \pm |^2\Pi_{-3/2}\rangle) \quad (10c)$$

Components of the rotational energy Hamiltonian  $H_{ROT}$  and the spin-orbit interaction Hamiltonian  $H_{SO}$  couple states of different electronic character, and cause the mixing of the zero-order wavefunctions which is the origin of perturbations. The perturbation interaction has been described by Lefebvre-Brion (1974) with two terms

$$\alpha = \frac{1}{2} \langle \Pi, v' | A L_+ | \Sigma, v \rangle \quad (11)$$

$$\beta = \langle \Pi, v' | B(R) L_+ | \Sigma, v \rangle \quad (12)$$

which contain the operator  $L_+$  and couple states of  $\Sigma$  and  $\Pi$  form through a spin-orbit (A) and rotation-electronic (B) interaction.

The matrix elements for the  $e$  and  $f$  parity sublevels of the  $X^2\Sigma$  state are given by the expression

$$\begin{aligned} \langle X^2\Sigma_{1/2} | X^2\Sigma_{1/2} \rangle = & T + B(x \mp 1) - D[x^2(x \mp 1)^2] + H[x^3(x \mp 1)^3] \\ & - \frac{1}{2}\gamma(1 \mp x) - \frac{1}{2}\gamma_D(1 \mp x)J(J+1) - \frac{1}{2}\gamma_H(1 \mp x)J^2(J+1)^2 \end{aligned}$$

where  $x = (J + \frac{1}{2})$ ; when a sign is given, the upper sign refers to the  $e$  sublevels and the lower one refers to the  $f$  sublevels. Nondegenerate perturbation theory is inadequate to describe the interactions between the  $A^2\Pi$ ,  $B^2\Sigma$ , and  $B'^2\Sigma$  states and consequently the perturbing levels are taken out of the Van Vleck summations and included explicitly in the Hamiltonian. The matrix elements for the  $A^2\Pi$ ,  $B^2\Sigma$ , and  $B'^2\Sigma$  states are given in Table 4.

#### 4. ANALYSIS AND DATA REDUCTION

Molecular parameters are determined by directly fitting the data using deperturbation methods. The procedure and the computer code follow the methods outlined by Field (1971), Albritton *et al* (1976), and Lefebvre-Brion and Field (1986). Line positions are directly computed from term values of the upper and lower state which are determined by diagonalization of the secular determinant of the model Hamiltonian. Trial parameters are taken from previous works or extrapolations in vibrational or rotational parameters and used to refine the spectroscopic identification of each line position. A nonlinear least square fitting procedure allows the molecular parameters to be adjusted until an satisfactory fit is achieved.

Spectroscopic identification and classification of rotational lines is performed by fitting each branch to a polynomial in  $J$  using the interactive computer code ANALYSIS (Pecyner and Davis (1988)). Such a fitting method is vital for following the development of each branch and correctly identifying perturbations. Lines which deviate from the expected position by more than three standard deviations ( $3\sigma$ ) are purged from the fit before the fit is recalculated. The branches of each band are then fit simultaneously with the nonlinear fitting algorithm NLFIT, used in previous analyses of diatomic spectra, to refine initial parameters for each band and to identify perturbed or misidentified lines (Abrams *et al* (1992)).

A global fit is then used to derive equilibrium parameters. In this fit all lines are used in the successive iterations (no lines are purged as the fit progresses). In each case trial parameters are developed and used to set up the Hamiltonians of the upper and lower states. Diagonalization generates the  $F_1$  and  $F_2$  sublevels for each  $J$ -value of the upper and lower states, from which calculated line positions are obtained for the transitions. Direct comparison of the calculated wavenumbers with the corresponding experimentally observed line positions generates corrections to the molecular parameters from which a new set of term values is calculated and the procedure is repeated until convergence is achieved. The final global fit of 2129 lines yielded a standard deviation of  $0.058 \text{ cm}^{-1}$ , which is an improvement over the previous result of  $0.11 \text{ cm}^{-1}$  for 1818 lines (Martin (1984)).

Deperturbed parameters for the  $X^2\Sigma$ ,  $A^2\Pi$ ,  $B^2\Sigma$ , and  $B'^2\Sigma$  states are given in Table 5. Interaction parameters describing the effects in the  $A^2\Pi(v_A)/B^2\Sigma(v_B)$  interaction are given in Table 6. A comparison with the results of Martin reveals two major differences: he did not include any  $\Lambda$ -type doubling parameters for the  $A^2\Pi$  state, whereas they are fully determined in this work. Consequently the  $B$  values of the  $B^2\Sigma$  state differ significantly. Secondly, the values of  $H_{BB'}$  obtained in this work are  $H_{10} = 13.8 \text{ cm}^{-1}$  and  $H_{20} = 30.6 \text{ cm}^{-1}$ , whereas Martin obtained  $7 \text{ cm}^{-1}$  and  $23 \text{ cm}^{-1}$  respectively in a semiempirical fit.

## CONCLUSIONS

We report the measurement of 2129 spectral lines of the red and orange systems of calcium hydride, including new transitions in the  $\Delta v = -1$  sequence of the  $A^2\Pi - X^2\Sigma$  band and the 2-3 band of the  $B^2\Sigma - X^2\Sigma$  band system which have been analyzed to obtain deperturbation parameters for the  $X^2\Sigma$ ,  $A^2\Pi$ , and  $B^2\Sigma$  states. A global fit has

been performed to a Hamiltonian including the near degenerate  $B'^2\Sigma$  electronic state explicitly. A standard deviation of  $0.058\text{ cm}^{-1}$  is obtained for the nonlinear least square fit of 2129 lines to 90 parameters including the  $\Lambda$ -type doubling parameters for the  $A^2\Pi$  state.



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Table 1  
0-1 Band of A-X System

J	P11	P22	R11	R22
.5				13210.74212
1.5				13216.83478
2.5				13223.60819
3.5		13159.11368	13183.78680	13230.98238
4.5	13113.76390	13149.42175	13195.97286	13238.90783
5.5	13109.54919	13140.33379	13208.08407	13247.31951
6.5	13105.28483	13131.93191	13220.21643	13256.24285
7.5	13101.04524	13124.05767	13232.38114	13265.46702
8.5	13096.86166	13116.70380	13244.63031	13275.27382
9.5	13092.78035	13109.85142	13256.96189	13285.36884
10.5	13088.85402	13103.49874	13269.41510	13295.81912
11.5	13085.10322	13097.60024	13282.01086	13306.60576
12.5	13081.56548	13092.14897	13294.76199	13317.72258
13.5	13078.23088	13087.15690	13307.72236	13329.14047
14.5	13075.22665	13082.59544	13320.76483	13340.83395
15.5	13072.47064	13078.46842	13334.03760	13352.88538
16.5	13069.96549	13074.76922	13347.49120	13365.17571
17.5	13067.87340	13071.50714	13361.13916	13377.76771
18.5	13066.05082	13068.68954	13374.99859	13390.61561
19.5	13064.58914	13066.26958	13389.04838	13403.73698
20.5	13063.44998	13064.33266	13403.29874	13417.11975
21.5	13062.68698	13062.78611	13417.75307	13430.75266
22.5		13061.72288	13432.44277	13444.66400
23.5	13062.29706	13061.11217	13447.28963	13458.80470
24.5		13060.87626	13462.37455	13473.20260
25.5			13477.64832	13487.84348
26.5		13061.82743	13493.13543	13502.71936
27.5	13066.26958	13062.97318	13508.82658	13517.84385
28.5		13064.58914		13533.17180
29.5	13070.63034	13066.65515		13548.75896
30.5	13073.47488	13069.17447		
31.5	13076.74204	13072.16532		13580.65754
32.5	13080.45554	13075.61114		13596.86881
33.5	13084.58674	13079.50977		13613.31132
34.5	13089.18990			13629.98231
35.5				13646.80427
36.5	13099.70438			13663.90654

Table 1  
0-1 Band of A-X System

J	Q11	Q22	Q12	Q21
1.5			13121.94897	
2.5			13118.05011	
3.5			13114.10384	
4.5	13147.53103		13109.85142	
5.5	13151.35110	13191.36177	13105.61900	13238.65316
6.5	13155.35508	13192.59934	13101.33311	13247.04712
7.5	13159.59416	13194.49170	13097.20261	13255.91420
8.5	13164.09847	13197.03325	13093.17517	13265.12247
9.5	13168.89444	13200.18570	13089.18990	13274.89113
10.5	13173.99874	13203.92330	13085.57725	13284.91778
11.5	13179.43481	13208.21945		13295.34259
12.5	13185.21388	13213.04216		13306.08543
13.5	13191.36177	13218.38544	13075.83149	
14.5	13197.83898	13224.22466	13073.10586	
15.5	13204.70069	13230.55166	13070.63034	
16.5	13211.93399	13237.34746	13068.68954	
17.5	13219.54582	13244.63031	13066.65515	
18.5	13227.53736	13252.32539		
19.5	13235.90815	13260.48563		
20.5	13244.63031	13269.08741		
21.5	13253.79735	13278.11721		
22.5	13263.30928	13287.56932		
23.5	13273.21220	13297.44501		
24.5	13283.49054	13307.72236		
25.5	13294.14294	13318.42407		
26.5	13305.17881	13329.52187		
27.5	13316.58493	13341.00035		
28.5	13328.36562	13352.88538		
29.5	13340.52097	13365.17571		
30.5	13353.02037	13377.76771		
31.5	13365.88461	13390.90111		
32.5	13379.13509	13404.23177		
33.5	13392.71901	13417.99147		
34.5	13406.63403	13432.11641		
35.5	13420.94051	13446.58742		
36.5	13435.94466	13461.41789		
37.5	13450.53298			
38.5	13466.25392	13492.10520		
39.5		13507.74059		

Table 1  
1-2 Band of A-X System

J	P11	P22	R11	R22
8.5		13190.93091	13314.99486	
9.5		13184.30718	13326.88362	13355.33356
10.5	13162.94629	13177.93918	13338.89494	13365.38930
11.5	13159.11368	13172.04142	13351.05529	13375.84013
12.5	13155.52666	13166.59555	13363.37662	13386.51560
13.5	13152.18404	13161.61068	13375.84013	13397.55616
14.5	13149.11196	13157.04536	13388.55687	13409.03717
15.5	13146.32929	13152.93511	13401.43601	13420.54104
16.5	13143.86404	13149.42175	13414.50465	13432.58554
17.5	13141.71211		13427.76122	
18.5	13139.88755			

Table 1  
1-2 Band of A-X System

J	Q11	Q22
4.5	13220.80965	
5.5	13224.57614	13265.54191
6.5	13228.51313	13266.65171
7.5	13232.67900	13268.44623
8.5	13237.10254	13270.87052
9.5	13241.81422	13273.89765
10.5	13246.83242	13277.49827
11.5	13252.16736	13281.63803
12.5	13257.83621	13286.31091
13.5	13263.85087	13291.48345
14.5	13270.21707	13297.14970
15.5	13276.94357	13303.29784
16.5	13284.03290	13309.90502
17.5	13291.48345	13316.96881
18.5	13299.32244	13324.48116
19.5	13307.50730	13332.42643
20.5	13316.07289	13340.83395
21.5	13325.01272	13349.60370
22.5		13358.82066
23.5		13368.44603

Table 1  
2-3 Band of A-X System

J	P11	P22	R11	R22
4.5			13337.64142	
5.5	13255.50799		13348.83375	13387.93892
6.5	13251.25960		13360.22522	13396.13592
7.5	13247.04712	13270.51528	13371.51097	13404.74981
8.5	13242.72967	13263.30928	13382.88615	13413.77170
9.5	13238.56392	13256.49980	13394.37020	13423.19066
10.5	13234.55272	13250.20508	13405.96648	13432.90538
11.5	13230.75113	13244.38402	13417.75307	13442.96285
12.5	13227.13707	13238.90783	13429.69783	13453.35959
13.5	13223.81848	13234.08576	13441.80511	13464.06974
14.5	13220.80965	13229.59904	13454.16955	13475.05966
15.5	13218.00491	13225.54165	13466.71097	13486.34702
16.5	13215.58007	13221.91800	13479.44939	13497.91093
17.5	13213.49190	13218.70838	13492.38382	13509.75675
18.5	13211.71684	13215.93400	13505.53401	13521.85785
19.5	13210.33170	13213.49190	13518.88294	13534.22082
20.5	13209.29260		13532.43909	13546.83394
21.5	13208.61918		13546.19373	13559.68594
22.5				13572.78180
23.5	13208.21945			13586.11887
24.5				13599.66384

Table 1  
2-3 Band of A-X System

J	Q11	Q22
5.5		13337.11741
6.5		13338.16068
7.5	13303.43166	13339.86952
8.5	13307.72236	13342.18554
9.5	13312.41414	13345.09702
10.5	13317.34487	13348.56884
11.5	13322.58351	13352.57604
12.5	13328.14428	13357.10119
13.5	13334.03760	13362.12060
14.5	13340.28166	13367.62780
15.5	13346.88160	13373.60888
16.5	13353.82542	13380.04207
17.5	13361.13916	13386.92221
18.5	13368.79190	13394.23551
19.5	13376.82038	13401.98740
20.5	13385.21802	13410.15656
21.5	13393.95802	13418.74235
22.5	13403.07260	13427.76122
23.5	13412.55354	

Table 1  
2-3 Band of B-X System

J	P11	P22	R11	R22
10.5	14468.21954	14473.05507	14640.96152	14661.77152
11.5	14464.95877	14470.25116	14653.51196	14675.11513
12.5	14462.22854	14467.98015	14666.45014	14688.57036
13.5	14459.70091	14466.15100	14679.41156	14702.37948
14.5	14457.52218	14464.74701	14692.59915	14716.21111
15.5	14455.54184	14463.77375	14705.77473	14730.21028
16.5	14454.16114	14463.05658	14719.39849	14744.36271
17.5	14452.71060	14462.61500	14733.13034	
18.5	14451.59400		14746.62047	
19.5	14450.74528			
20.5	14450.41607			



**Table 3**  
**Second- and Third- Order Matrix Elements for the UPA Hamiltonian**

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$$\begin{aligned}
D_v &= - \sum_{v'} \frac{|\langle v' | B(r) | v \rangle|^2}{E_v - E_{v'}} \\
p_v &= 2 \sum_{v'} \frac{\langle v' | A(r) L_+ | v' \rangle \langle v | B(r) L_+ | v' \rangle}{E_v - E_{v'}} \\
q_v &= 2 \sum_{v'} \frac{|\langle v' | B(r) L_+ | v \rangle|^2}{E_v - E_{v'}} \\
o_v &= \sum_{v'} \frac{|\langle v' | A(r) L_+ | v \rangle|^2}{E_v - E_{v'}} \\
\gamma_{Dv} &= \sum_{v'} \frac{\langle v' | \gamma(r) | v' \rangle \langle v | B(r) | v' \rangle}{E_v - E_{v'}} \\
A_{Dv} &= 2 \sum_{v'} \frac{\langle v | A(r) | v' \rangle \langle v | B(r) | v' \rangle}{E_v - E_{v'}} \\
H_v &= \sum_{v' \neq v} \sum_{v'' \neq v} \frac{\langle v' | B(r) | v \rangle \langle v' | B(r) | v'' \rangle \langle v'' | B(r) | v \rangle}{(E_v - E_{v'})(E_v - E_{v''})} - \langle v | B(r) | v \rangle \sum_{v' \neq v''} \frac{|\langle v | B(r) | v' \rangle|^2}{(E_v - E_{v'})^2}
\end{aligned}$$


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Table 4

Matrix Elements for the  $A^2\Pi$ ,  $B^2\Sigma$ , and  $B'^2\Sigma$  States of CaH  
Evaluated in an  $e/f$  Symmetrized, Hund's case (a) Basis Set

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$$\begin{aligned}
 \langle A^2\Pi_{1/2} | A^2\Pi_{1/2} \rangle &= T - \frac{A}{2} - A_D x^2 \\
 &\quad + Bx^2 + D[1 - x^4 - x^2] + H[x^6 + 3(x^2 - 1)^2 + x^2 - 1] \\
 &\quad + \frac{p}{2}[1 \mp x] + \frac{pD}{2}[1 \mp x]J(J+1) \\
 &\quad + \frac{q}{2}[1 \mp x]^2 + \frac{qD}{2}[1 \mp x]^2 J(J+1) + \frac{qH}{2}[1 \mp x]^2 J^2(J+1)^2 \\
 \langle A^2\Pi_{3/2} | A^2\Pi_{3/2} \rangle &= T + \frac{A}{2} + A_D(x^2 - 2) \\
 &\quad + B(x^2 - 2) + D[1 - x^2 - (x^2 - 2)^2] + H[(x^2 - 2)^3 + 3(x^2 - 1)^2 - x^3 + 1] \\
 &\quad + \frac{q}{2}[x^2 - 1] + \frac{qD}{2}[x^2 - 1]J(J+1) + \frac{qH}{2}[x^2 - 1]J^2(J+1)^2 \\
 \langle A^2\Pi_{3/2} | A^2\Pi_{1/2} \rangle &= -B(x^2 - 1)^{1/2} + 2D(x^2 - 1)^{3/2} - H(x^2 - 1)^{1/2}[3(x^2 - 1)^2 + x^2] \\
 &\quad + \frac{p}{4}(x^2 - 1)^{1/2} - \frac{pD}{4}(x^2 - 1)^{1/2}J(J+1) \\
 &\quad - \frac{q}{2}[1 \mp x](x^2 - 1)^{1/2} - \frac{qD}{2}[1 \mp x](x^2 - 1)^{1/2}J(J+1) \\
 &\quad - \frac{qH}{4}[1 \mp x](x^2 - 1)^{1/2}J^2(J+1)^2 \\
 \langle B^2\Sigma_{1/2} | B^2\Sigma_{1/2} \rangle &= T + B(x \mp 1) + D[x^2(x \mp 1)^2] + H[x^3(x \mp 1)^3] \\
 &\quad - \frac{1}{2}\gamma(1 \mp x) - \frac{1}{2}\gamma_D(1 \mp x)J(J+1) - \frac{1}{2}\gamma_H(1 \mp x)J^2(J+1)^2 \\
 \langle B^2\Sigma_{1/2} | A^2\Pi_{1/2} \rangle &= \alpha + \beta(1 \mp x) \\
 \langle B^2\Sigma_{1/2} | A^2\Pi_{3/2} \rangle &= -\beta(x^2 - 1)^{1/2} \\
 \langle B^2\Sigma_{1/2} | B'^2\Sigma_{1/2} \rangle &= H_{BB'} \\
 \langle B'^2\Sigma_{1/2} | B'^2\Sigma_{1/2} \rangle &= T + BJ(J+1) - D(J^2(J+1))^2
 \end{aligned}$$


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The matrix elements are given for the  $e$  and  $f$  parity sublevels with  $x = (J + \frac{1}{2})$ . When a sign is given, the upper sign refers to the  $e$  sublevels and the lower one refers to the  $f$  sublevels.

Table 5a  
Molecular Parameters for the  $A^2\Pi$  State of  $\text{CaH}^a$

$v$	0	1	2	3
$T_v$	14429.8280(59)	15725.3903(92)	16980.174(16)	18194.558(52)
$A_v$	79.804(12)	79.845(14)	79.879(24)	79.907(93)
$B_v$	4.347439(70)	4.244360(85)	4.140588(126)	4.03398(58)
$D_v \times 10^4$	1.89099(76)	1.88180(119)	1.8517(18)	1.6946(167)
$H_v \times 10^9$	5.472(28)	5.097(54)	[1.148]	[.505]
$A_D \times 10^3$	-2.514(20)	-3.036(26)	-3.621(62)	-9.51(40)
$p_v$	-.72951(74)	-.7091(16)	-.7484(26)	-.7775(72)
$p_D \times 10^5$	10.587(68)	7.92(11)	8.07(27)	6.5(20)
$q_v \times 10^2$	-7.2036(36)	-6.797(11)	-6.477(23)	-6.164(61)
$q_D \times 10^5$	1.3225(60)	1.226(13)	.935(42)	.35(20)
$q_H \times 10^9$	-1.632(25)	-1.676(58)	1.62(27)	-10.3(18)

<sup>a</sup> All values are given in reciprocal centimeters, and the error quoted is one standard deviation in the last decimal place. Bracketed quantities are held constant during the fitting process.

**Table 5b**  
**Molecular Parameters for the  $B^2\Sigma$  State of CaH<sup>a</sup>**

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$v$	0	1	2
$T_v$	15753.7211(98)	16997.978(22)	18189.901(96)
$B_v$	4.41205(12)	4.29273(23)	4.16200(34)
$D_v \times 10^4$	2.1598(13)	2.2059(44)	2.4874(90)
$H_v \times 10^9$	6.367(48)	4.28(31)	[1.51]
$\gamma$	-.70994(86)	-.7507(14)	-.8463(32)
$\gamma_D \times 10^5$	[4.35]	[5.17]	[2.27]

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<sup>a</sup> All values are given in reciprocal centimeters, and the error quoted is one standard deviation in the last decimal place. Bracketed quantities are held constant during the fitting process.

**Table 5c**  
**Molecular Parameters for the  $X^2\Sigma$  State of  $\text{CaH}^a$**

$v$	0	1	2	3
$T_v$	0.0	1260.0983(79)	2481.952(14)	3665.321(19)
$B_v$	4.227758(69)	4.130903(74)	4.03354(14)	3.93557(15)
$D_v \times 10^4$	1.83173(67)	1.83120(87)	1.8368(35)	1.8473(23)
$H_v \times 10^9$	5.284(21)	5.299(34)	5.80(28)	[6.10]
$\gamma$	.03824(69)	.03710(71)	.03574(92)	.0349(16)
$\gamma_D \times 10^5$	1.62(13)	1.32(17)	1.27(16)	1.22(48)
$\gamma_H \times 10^8$	-1.533(59)	-1.289(98)	[-1.213]	[-1.213]

<sup>a</sup> All values are given in reciprocal centimeters, and the error quoted is one standard deviation in the last decimal place. Bracketed quantities are held constant during the fitting process.

**Table 6 Interaction Parameters for the  $A^2\Pi$  and  $B^2\Sigma$  States of CaH**

$v$	$A_1/B_0$	$A_2/B_1$	$A_3/B_2$
$\alpha$	.557(37)	-.859(34)	-3.058(29)
$\beta$	.6930(29)	.8534(29)	.8296(24)

<sup>a</sup> All values are given in reciprocal centimeters, and the error quoted is one standard deviation in the last decimal place.